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Convenient Molecular Approach of Size and Shape Controlled ZnSe and ZnTe Nanocrystals

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ABSTRACT

Our study describes a convenient one-step synthesis of ZnSe and ZnTe nanocrystals (NC) whose sizes and shapes are precisely tuned by varying the growth temperature or stabilizing surfactants. We utilized molecular precursors, bis(phenylselenolate or phenyltelluroato)zinc -N,N,N',N'-tetramethylethylenediamine (TMEDA), which effectively produce 0-dimensional sphere or 1-dimensional nanorods of ZnSe or ZnTe, respectively. Nanocrystals are highly monodispersed and luminescent; the emission wavelength varies over a wide range depending on the particle size. This study constitutes a nice demonstration of direct size and shape controlled synthesis of semiconductor nanocrystals and this method can be extended to the synthesis of nanocrystals of other materials.

INTRODUCTION

Controlled synthesis of inorganic nanocrystals is one of the most important issues in nanocommunity because their size and shape act as important parameters for optical and electronic properties. Especially, 1-dimensional nanocrystals have drawn special attention because of novel properties due to their anisotropic crystal structure [1, 2].

Shape control of nanocrystals can be achieved in gas phase by several methods. One of the methods is template-assisted or strain-assisted synthesis in gas phase. For example, crystal growth inside a nanoporous solid, such as silica ball template, MCM-41, leads to the formation of nanorods, nanowires, and nanoballs [3, 4]. Pyramidal dots or nanowires can be obtained using strain-assisted epitaxial growth [5]. Lieber et al. reported that a solid rod can be obtained using vapor-liquid-solid growth [6] and Buhro et al. demonstrated solid rods also obtained by solution-liquid-solid growth [7].

The other means of controlling nanocrystals is colloidal synthesis using micelle templates. Mann et al. show that prismatic BaCrO_4 nanocrystals can be obtained by introducing Ba^{2+} and CrO_4^{4-} ion in AOT microemulsion using structured AOT micelles [8]. Nanorods were prepared by electrochemical reduction method [9], hydrazine reduction method [10], and simple ionic reactions [11]. Recently, a nonhydrolytic synthesis of CdSe nanorods in hot mixture of trioctylphosphine oxide and hexylphosphonic acid was reported [1].

In this paper, we demonstrate size and shape controlled ZnE (E=Se, Te) nanocrystals with quantum confinement effects. Shape of zinc chalcogenide nanocrystals is controllable either spherical or rod-like structure depending on the choice of stabilizing surfactants. Furthermore, the size of spherical nanocrystals is controlled by the growth temperature.

EXPERIMENTS

Trioctylphosphine (Aldrich) was used as received, while trioctylamine, and dimethylhexylamine were distilled before use. Trioctylphosphine oxide (TOPO) dodecylamine (Aldrich) were dried and degassed before use in the reaction vessel by heating $\sim 200^{\circ}\text{C}$ at ~ 1 Torr for ~ 2 hr with argon gas bubbling. $\text{Zn}(\text{SePh})_2(\text{TMEDA})$ [12] and $\text{Zn}(\text{TePh})_2(\text{TMEDA})$ [13] were prepared following a literature method.

Low resolution transmission electron microscope image, energy dispersive X-ray analysis (EDAX), and selected area electron diffraction (SAED) were performed on an EM 912 Omega electron microscope operating at 120 kV. High resolution transmission electron microscope (HRTEM) images were obtained on a Hitachi H9000-NAR high resolution TEM operating at 300 kV. The UV-Vis absorption spectra of ZnTe anocrystals were obtained with a Shimadzu UV-3100S spectrophotometer and photoluminescence spectra were obtained with a Perkin-Elmer LS50 Luminescence spectrometer. X-ray powder diffraction patterns were measured on a Rigaku Miniflex instrument (0.5 kW) operating with a $\text{Cu K}\alpha$ ($\lambda = 0.1541 \text{ nm}$) X-ray source.

ZnSe Nanocrystals. $\text{Zn}(\text{SePh})_2(\text{TMEDA})$ (0.5 g, 0.101 mmole) was dissolved in trioctylphosphine (10 ml) and the resulting solution was injected into hot trioctylphosphine oxide (3.92 g, 10.1 mmol). The latter solution was kept at one of four different temperatures: 320, 340, 367, or 385°C . After 1 hr, the resulting yellow solution was cooled to 80°C and treated with an excess of methanol to generate a yellow flocculate, which was separated by centrifugation and washed with methanol. The resulting pale yellow powder was readily redispersed in toluene.

ZnTe Nanocrystals. $\text{Zn}(\text{TePh})_2(\text{TMEDA})$ (0.50 g, 0.88 mmol) was dissolved in 5 ml of trioctylphosphine and the resulting solution was injected into hot trioctylamine (8.17 g, 44.1 mmol) solvent. The reaction mixture was kept at two different temperatures: 180 or 240°C . After 2 hr, the resulting yellow solution was cooled to 40°C and treated with an excess of anhydrous butanol to generate a yellow flocculate, which was separated by centrifugation and washed with butanol. The resulting a pale yellow powder was dispersed in organic solvents such as toluene.

ZnTe Nanorods. $\text{Zn}(\text{TePh})_2(\text{TMEDA})$ (0.50 g, 0.88 mmol) was dissolved in 5 ml of pyridine and the resulting solution was injected into hot mixture of trioctylamine (20 ml) and dimethylhexylamine (5 ml). The reaction mixture was kept at 180°C . After 2 hr, the resulting yellow solution was treated with an excess of anhydrous butanol to generate a gray flocculate, which was separated by centrifugation and washed with butanol. The resulting nanocrystals are obtained as a gray powder.

RESULTS AND DISCUSSION

Zinc chalcogenide nanocrystals were obtained by the thermolysis of $[\text{Zn}(\text{EPh})_2][\text{TMEDA}]$. According to thermal gravimetric analysis (TGA), it is observed that the thermolysis of $[\text{Zn}(\text{EPh})_2][\text{TMEDA}]$ begins with the dissociation of the TMEDA donor ligand and then ZnE and Ph_2E are produced in the following thermolysis step at higher temperatures.

Obtained spherical ZnSe nanocrystals are highly monodispersed with sizes that depend on the growth temperature. Relative to the position of the 480 nm (2.58 eV) absorption band edge for bulk ZnSe, the absorption band edges of the ZnSe QDs are blue-shifted. The absorption band shifts are 1.07, 0.49, 0.41 and 0.29 eV for QDs grown at 385, 367, 340 and 320 °C, respectively. The band maxima in photoluminescent spectra are 387 nm (3.20 eV), 429 nm (2.89 eV), 443 (2.80 eV) and 451 nm (2.75 eV) for samples grown at 380, 367, 340 and 320 °C, respectively (Fig. 1A). In case of spherical ZnTe nanocrystals, similar behaviors were observed. Relative to the position of the 548 nm (2.26 eV) absorption band edge of bulk ZnTe, blue shifts are 0.53 and 1.31 eV for the nanocrystals grown at 180 and 240 °C, respectively. The band maxima in photoluminescent spectra are 451 and 377 nm for samples grown at 180 and 240 °C (Figure 2A). Larger shifts are seen for samples grown at higher growth temperature in both cases. These results suggest that smaller nanocrystals are produced at higher growth temperatures where more nucleation sites exist and relatively less available zinc chalcogenide precursor molecules are present for each nucleus during the growth process.

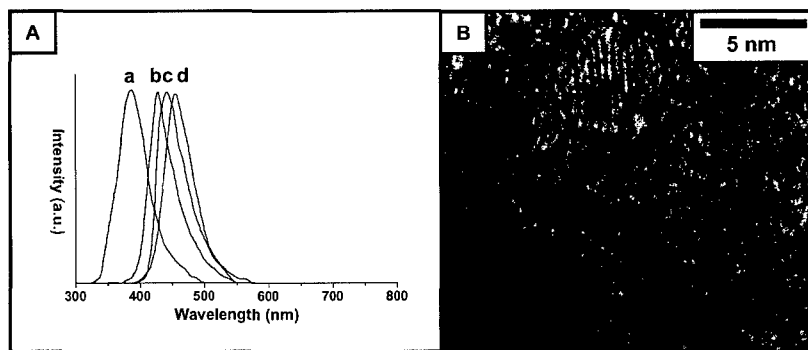


Figure 1. Spherical ZnSe nanocrystals (A) PL spectra ZnSe NCs grown at (a) 385, (b) 367, (c) 340, and (d) 320 °C. (B) HRTEM image of 4.9 nm ZnSe NCs

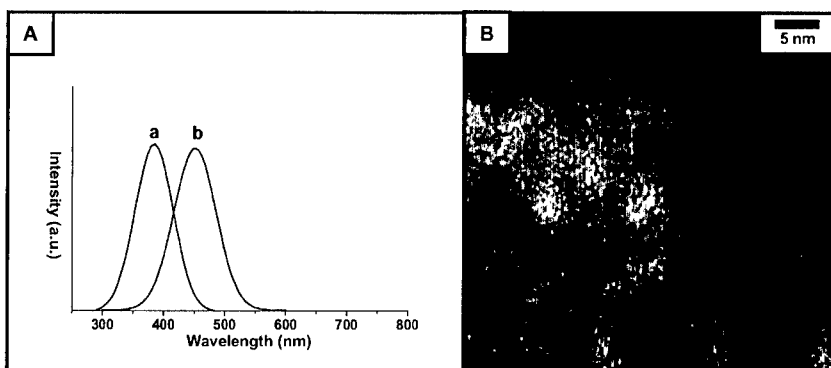


Figure 2. Spherical ZnTe nanocrystals (A) PL spectra ZnTe NCs grown at (a) 240 and (b) 180 °C, (B) HRTEM image of 4.2 nm ZnTe NCs

High resolution transmission electron micrographs show that the zinc chalcogenide nanocrystals are roughly spherical and that the particles within a single sample have relatively uniform sizes. The average sizes of the ZnSe QDs are 2.7 (\pm 0.2) nm, 4.0 (\pm 0.35) nm, 4.4 (\pm 0.35) and 4.9 (\pm 0.29) nm for samples grown at 385, 367, 340, 320 °C (Figure 1A) and ZnTe nanocrystals have average sizes of 4.2 (\pm 1.1) and 5.4 (\pm 0.9) nm for samples grown at 240 and 180 °C, respectively (Figure 2B). Powder X-ray diffractometry (XRD) and selected area diffractometry (SAED) reveal patterns corresponding to (111), (220) and (311) of the cubic phase of ZnTe nanocrystals.

With the same conditions and procedures, the injection of the precursor $[\text{Zn}(\text{TePh})_2][\text{TMEDA}]$ into the mixed surfactant solvents of trioctylamine (20 ml) and dimethylhexylamine (5 ml) leads to the shape change of the nanocrystals from spherical to rod-like shape and after 2 hr gray precipitates of ZnTe nanocrystals are obtained from initially pale yellow solution at 180 °C. It is believed that the combination of two different surfactants provides rod micelles during one-dimensional crystal growth process.

TEM image of rod-like ZnTe nanocrystals show that the nanocrystals have relatively larger size than spherical nanocrystals (Figure 3A). The diameters of the rod-like nanocrystals are uniform with \sim 25 nm and the lengths are several hundred nanometers (200 \sim 700 nm) with aspect ratio from 8 to 30. Figure 3B, C show SAED patterns of single ZnTe nanorod. Our rod-like ZnTe nanocrystals have well defined single crystallinity with cubic phase according to the electron diffraction study. The intensity of diffraction patterns varies depending on the crystallographic directions; the intensity of electron diffraction spots is increasingly stronger from 002 to 220 plane, which indicates that the ZnTe crystals are formed in unidirectional crystal growth pattern of ZnTe 110 face.

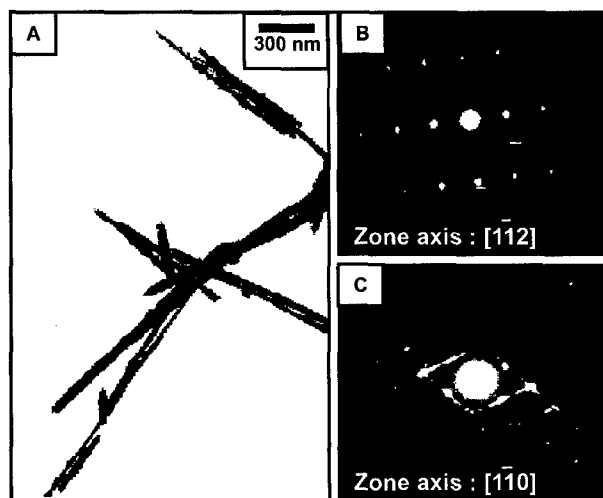


Figure 3. ZnTe nanorods (A) HRTEM image, (B) and (C) SAED pattern with zone axis

CONCLUSION

The results in this paper constitute a simple and convenient one-pot synthesis of size and shape controlled zinc chalcogenide nanocrystals using a monomeric molecular precursor, $[\text{Zn}(\text{EPh})_2][\text{TMEDA}]$. By varying the growth temperature or the choice of the templating surfactants, the size and shape of the nanocrystals are controllable and quantum size effects are observed.

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